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KINETICS OF ENERGETIC SPECIES
AT LOW TEMPERATURES

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Seymour Siegel, Ph.D.

AEROJET-GENERAL CORPORATION
Azusa, California

Aerojet-General Report
No. 2121 (Final)

Contract No. AF 18(603)-110

NOVEMBER 1961

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
Washington, D.C.



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FOREWORD

This Technical Report completes the fulfillment of work under the contract and is submitted in accordance with the mandatory requirements of ARDC Manual 5-1. It covers the period from 1 October 1959 through 30 September 1961.

Approved by:


D. L. Armstrong
Director of Chemistry

ABSTRACT

Research during the past 2 years on the stabilization and subsequent chemical reactions of energetic free radicals is summarized. Hydrogen atoms, hydroxyl radicals, and other normally unstable chemical species, produced by ionizing radiation and by electric discharges, were stabilized at low temperatures and were subsequently investigated.

The rates of formation and disappearance of some of these radicals were measured over a range of temperatures by means of electron-paramagnetic-resonance techniques. Mechanisms are postulated to explain the observed rate phenomena.

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I. INTRODUCTION

This report summarizes the more important results obtained in the past 2 years of research on the stabilization and subsequent chemical reactions of energetic free radicals in solid matrices at low temperatures.

The results of research conducted in this program prior to 1 October 1959 are covered in two previous technical-summary reports (Refs. 1 and 2)* and in a number of publications, presentations, and Technical Notes (Refs. 3 through 15). Research accomplishments during the past 2 years, which are presented in this report, have led to the publication of three papers in the open literature (Refs. 16 through 18), and to the presentation of a paper at the Fifth International Symposium on Free Radicals (Ref. 19). A fourth paper has been submitted to the Journal of Chemical Physics, and an additional paper has recently been completed. Because the published material has also been issued in the form of Technical Notes (Refs. 20 through 23), this report consists only of an overall summary.

During the 2-year period covered by this report, the investigations were concerned primarily with the kinetics of radical-formation reactions during the beta- and gamma-irradiation of ice at 4.2 and 77°K and with the mechanism of disappearance of radicals, especially hydrogen atoms, when the γ -irradiated ice is warmed from 4.2°K to higher temperatures. These investigations led to the postulation of mechanisms for the formation and decomposition of radicals in

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*References are listed in the Bibliography presented at the end of this report. The Bibliography is preceded by a List of Technical Notes.

ice at low temperatures and to an experimental test of decomposition. A previously reported isotope effect (Ref. 21) in the formation of hydrogen and deuterium atoms in irradiated "mixed" ice at 4.2°K was studied in detail. Exploratory investigations were also conducted on radicals formed from and trapped in other solid matrices at low temperatures. Detection and concentration measurements of the trapped radicals were accomplished by means of electron-paramagnetic-resonance (EPR) spectrometry.

II. BACKGROUND

A program to investigate the feasibility of utilizing trapped, energetic, molecular fragments - "free radicals" - as ultra-energy propellants for rocket propulsion was initiated at Aerojet-General in 1954. This early work was performed under Contract AF 18(600)-1216. The results of that program are summarized in Ref. 1.

The feasibility of the utilization of stabilized free radicals as ultra-energy propellants remains remote. In none of the studies under this program have concentrations of energetic radicals in excess of 1% been attained; the same is true of other laboratories. From experimental data recently determined, it may be inferred that concentrations above a few percent are not likely to be attained with present methods.

III. SUMMARY

A. PREVIOUS WORK

All the previous work under this contract was covered in detail in Refs. 1 and 2; hence, only the most pertinent details of the earlier investigations are given here.

1. Irradiated Ice at Low Temperatures

The spectra of ice irradiated at 4.2 and 77°K were resolved into components believed to be due to the H, OH, and HO_2 radicals. The H atoms were not stable in ice at 77°K .

The expected isotope effect on the spectrum attributed to the hydroxyl radical was observed in D_2O irradiated at 77°K .

The disappearance of OH in irradiated ice was found to be moderately rapid at 100°K, following a 3/2-order-reaction rate law. The activation energy for this process is 6.0 kcal/mole.

The γ -irradiation of ice at 77°K at a dose rate of about 10^5 rep/hr produced an ultimate stabilized OH concentration of about 6×10^{-4} moles/liter after 200 hr, although the initial rate of formation was about 6×10^{-5} mole/liter/hr ($G = 0.6$ molecule/100 ev), which is a factor of almost 4 smaller than the accepted value for OH formation in the irradiation of liquid H_2O .

Low concentrations of hydrogen atoms were stabilized at 77°K on a variety of surfaces.

Hydrogen atoms produced by the irradiation of wet Pyrex recombined rapidly at 100°K and followed a second-order-reaction rate law with an activation energy of 4 kcal/mole.

2. Radicals Trapped in Other Solid Matrices at Low Temperatures

Radicals believed to be CH_3 and CH_3O were trapped at 77°K from a high-frequency discharge in methanol.

Experiments designed to trap NH_2 radicals at 77°K from the mercury-photosensitized decomposition of NH_3 yielded only inconclusive results, because of contamination of the ammonia with mercury.

B. RECENT WORK

The results of investigations performed under this contract during the last 2 years are briefly summarized below.

1. Radical Formation in γ - and β -Irradiated Ice

It was concluded that the initial yields of stabilized OH radicals formed from 1.2-Mev γ -rays or from 5.7-Kev β -particles are the same.

It was shown, however, that the maximum concentration of OH radicals formed by the β -irradiation of ice was several times that formed by γ -irradiation.

A mechanism consistent with the observed rate of formation of radicals in ice at 77°K by γ - and β -irradiation was formulated. It assumes that for each ionization spur,* only one spatially separated radical pair is formed, and that all other pairs immediately recombine and are not influenced by previously stabilized radicals.

An isotope effect observed for relative yields of H and D atoms in the γ -irradiation of frozen H₂O and D₂O at 4.2°K was attributed to a difference in the efficiency of the H- and D-atom production. The yields of H and D atoms in "mixed" ice are in proportion to the yields in pure H₂O and D₂O.

2. Properties of Radicals in Irradiated Ice at Low Temperature

The decomposition of OH radicals formed in both γ - and β -irradiated ice follows a 3/2-order-reaction rate law whose rate constant may be written as

$$k = 3 \times 10^{11} \exp(-6000/RT) (\text{moles/liter})^{-1} \text{ sec}^{-1}$$

A mechanism based on the acidic dissociation of the OH radical was proposed to explain the observed kinetics.

The rate law for the decomposition of the OH radicals changed from that for a 3/2-order reaction to one for a second-order reaction upon the addition of excess H₂O₂, which is one of the products of the decomposition. These results were interpreted in terms of the postulated acidity of H₂O₂ in the frozen matrix.

Unsuccessful attempts were made to confirm the proposed mechanisms by inducing second-order-reaction rate kinetics upon the addition of HF or HCl to the frozen-water system.

At 4.2°K the initial H and OH radical yields from the γ -irradiation of ice are equal ($G_H \cong G_{OH} \cong 0.8/100 \text{ ev}$), whereas at 77°K no H radical is observed and $G_{OH} \cong 0.6/100 \text{ ev}$.

*"Spur" refers to a site of damage caused by ionizing radiation.

The mechanisms of the behavior of the H and OH radicals from γ -irradiated ice warmed from 4°K to 77°K are discussed in paragraph IV,B,2,b, following, in terms of their distribution, migration, and subsequent interaction within the frozen matrix.

A method was devised for maintaining a constant temperature between 4.2 and 77°K.

When the H radicals formed at 4.2°K in γ -irradiated ice were held at various constant temperatures between 20 and 50°K, the initial rapid rate of disappearance of these radicals was observed to asymptotically approach zero long before all the radicals had disappeared. This observation led to calculated activation energies ranging from 1 to 2.5 kcal/mole.

The kinetic data on the disappearance of the H and OH radicals from γ -irradiated ice led to the conclusions (a) that the reactions occurring in irradiated ice between 4.2 and 77°K may be primarily of the intra-spur type (in a given spur) rather than isotropic processes, and (b) that inter-spur reactions (between different spurs) should become increasingly important only in the last stages of the disappearance of the radicals.

3. Studies of Radiation Effects on Other Solid Matrices at Low Temperatures

The NF_2 radicals were not observed from the γ -irradiation of solid N_2F_4 or from the thermal dissociation of gaseous N_2F_4 ; this was attributed in part to the presence of impurities that may have combined with the NF_2 radical to form non-radical species.

The three-line spectrum from γ -irradiated ammonia was converted irreversibly to a 12-line spectrum on warming from 4.2 to 77°K. This change was interpreted in terms of a conversion of one radical into another.

A nine-broad-line radical spectrum was observed in γ -irradiated ethyl bromide at 77°K, but could not be identified. Upon warming to 150°K, the spectrum suddenly and irreversibly changed to that of the well-known ethyl radical.

The γ -irradiation of solid methyl iodide at 77°K produced methyl radicals, but ultraviolet irradiation produced almost no radicals. These phenomena were interpreted in terms of the almost-100% effectiveness of the cage effect for the ultraviolet case in preventing diffusion of the CH_3 and I radicals away from each other, whereas the γ -irradiation provides enough additional energy to permit the diffusion.

The stabilization of H atoms was observed on the surface of the quartz Dewar vessels used for ultraviolet-radiation studies of CH_3I , CH_3OH , and $(\text{CH}_3)_2\text{NNNN}(\text{CH}_3)_2$. The 3660-angstrom (Å) ultraviolet-radiation energy is less than that required to break a normal O-H, C-H, or N-H bond. Thus, the stabilization effect was attributed to chemisorption to the glass by some species, resulting in the weakening of the principal chemical bond to the hydrogen.

A dark red deposit was collected in a cold trap from discharged methanol. This deposit was attributed to either the CH_2^+ or CH_2OH radicals.

Different radical EPR spectra were observed for ultraviolet- and γ -irradiated methanol at 77°K.

It was concluded from the EPR spectra of condensed products from discharged tetramethyltetrazine (TMT) that the $(\text{CH}_3)_2\text{N}$ radical was not formed.

The paucity of radical concentration in methanol solutions of ultraviolet-irradiated TMT suggest that TMT is an excellent radical scavenger in methanol.

IV. TECHNICAL DISCUSSION

A. EXPERIMENTAL TECHNIQUES

The 1000-curie cobalt-60 source used for radical production by irradiation and the EPR spectrometer used for observing free radicals are described in detail in Refs. 2 and 5. The EPR spectrometer is described briefly below.

Electron-paramagnetic-resonance techniques can be used to detect, identify, and measure concentrations of species containing unpaired electrons; the perturbation of the system is minimal. A wide variety of species - such as F-centers (i.e., electrons trapped in a solid matrix) and atoms, ions, or molecules containing unpaired electrons - lend themselves to study by EPR techniques.

The EPR type of spectrometry is based on the slight difference in the population of spin states when electronic degeneracy is removed by a splitting of electronic levels in an applied magnetic field. The splitting is due to a parallel or antiparallel alignment of the unpaired electron spins with respect to the field. If energy of the proper frequency is applied, transitions can be made to occur between the electronic levels (i.e., the electron spins can be made to "flip-over" or change their orientation with respect to the field). In practice, it is found that optimum operating conditions occur at a magnetic field of about 3000 gauss. The "flip" or resonant frequency of a free (i.e., unbonded) electron spin at this value of field strength lies in the microwave region and is equal to approximately 9 kmc. When the electron is not free but is bonded to an atomic, ionic, or molecular species, the resonant frequency may change because of (1) nuclear or matrix perturbations, or (2) a coupling of the electron spin with the orbital angular momentum. In such cases it is desirable to scan the spectrum (i.e., to vary the field strength or resonant frequency so that resonant conditions are restored). In practice, this type of scan is accomplished by varying the magnetic field under conditions of constant frequency.

B. FORMATION AND DECOMPOSITION OF RADICALS IN ICE AT LOW TEMPERATURES

Ice was chosen as the main system for investigation in this radiation program because of (1) its importance in chemistry, and (2) the vast amount of literature available on the radiation chemistry of liquid water and free-radical yields in this system. The experimental approach consisted of freezing ice into an EPR cavity at 77°K, γ -irradiating, and scanning the EPR spectrum for evidence of free radicals. The first EPR studies showed that

hydrogen atoms and hydroxyl radicals were produced by the γ -irradiation of ice. The spectrum at 4.2°K contained the characteristic 500-gauss doublet of atomic hydrogen, whereas the 77°K spectrum did not. A 40-gauss doublet that was the main feature of the spectrum at 77°K was also present at 4.2°K. The doublet at 77°K was attributed to the coupling of an unpaired electron with a species containing a single proton. The irradiation of pure D₂O at 77°K yielded a triplet spectrum, as expected. These spectra were assigned to the OH and OD radicals, respectively. This assignment is now generally accepted, and additional experiments performed in other laboratories (Ref. 24) have provided additional support.

1. Radical Formation in γ - and β -Irradiated Ice

A detailed study of the rate of formation of OH in ice by γ -irradiation at 77°K indicated that initial radical yields ($G_{OH} = 0.6$ rad/100 ev) were directly proportional to the radiation dosage. These yields are approximately a factor of 4 lower than the yields in liquid water ($G_{OH} = 2.2$ rad/100 ev).^{*} Upon continued irradiation, however, it was shown that the OH yields did not increase in proportion to the radiation dosage and, upon prolonged irradiation, approached a maximum concentration of about 6×10^{-4} mole/liter. Moreover, it was found that the formation curve could be empirically fitted by

$$\frac{d(OH)}{dt} = a - b (OH)^{1/4}$$

This dependence upon the stabilized OH concentration is much less than the 3/2-order-reaction dependence observed for the isothermal decomposition of OH in ice.

a. Formation of OH Radicals in γ - and in β -Irradiated Ice at 77°K

In order to determine whether OH radicals produced by the 5.7-Kev β -particles from tritium decay would have a different spatial distribution in ice from that of radicals produced by the 500-Kev primary electrons formed during Co⁶⁰ γ -irradiation, and whether these differences in distribution would affect the kinetics of formation and decomposition of OH, a sample of tritium-enriched ice was maintained at 77°K and the rates of formation of the radicals were followed. It was hoped also that these experiments would determine

^{*}Ref. 25.

whether other short-lived intermediate paramagnetic species might be present during the irradiation. Such an experiment could not be performed with the Co^{60} source, because the nature of that facility prevents EPR observations during irradiation.

The rate of formation of hydroxyl radicals was observed for several weeks in the internally β -irradiated ice sample maintained at 77°K (see Figure 1 for the spectrum of OH). This rate was compared with rates previously observed in ice samples that were γ -irradiated by means of an external Co^{60} source (Ref. 16). The dose rate in the β -irradiation was about 0.7×10^{18} ev/g-hr (1.1×10^4 rep/hr), as compared with 5.3×10^{18} ev/g-hr (8×10^4 rep/hr) for the previous γ -irradiation experiments. The rates of formation were compared by plotting radical concentration against total irradiation dosage for the two cases (see Figure 2).

The initial rate of formation of hydroxyl radicals was found to be proportional to the dose rate for the two irradiation experiments (γ and β) within the estimated experimental error of approximately 15%. Therefore, the initial irradiation yields of stabilized OH (radicals/100 ev) at 77°K were concluded to be the same for irradiation with 5.7-Kev β -particles as for 1.2-Mev γ -rays.

Although the initial rates of formation of OH radicals per unit irradiation dosage at 77°K by the two different types of irradiation were found to be the same, the maximum concentration of OH radicals was found to be several times greater in the internally β -irradiated ice sample. The two formation curves (see Figure 2) also exhibit different functional dependences on the stabilized OH concentration.

Near the beginning of one of the β -irradiation studies, several very weak EPR absorption lines were observed that corresponded to none of the previously recorded spectra after γ -irradiation. These lines were barely observable after about 1 to 2 hr of irradiation and disappeared shortly thereafter. Because the maximum signal strength observed was so low, these studies were discontinued.

b. Proposed Mechanism for Radical Formation in Ice Matrices at 77°K

A mechanism was formulated that is consistent with the observed OH-radical formation in ice as a function of irradiation dosage. This mechanism assumes, as a crude approximation, that for each ionization spur only one spatially separated radical pair is formed; all other pairs immediately recombine and are not influenced by the background concentration of previously stabilized radicals. This assumption is based on the 4.2°K investigation, in which the yield was found to be about 1 pair/100 ev (Ref. 21). On the basis of this premise, a calculation can be made for the probability of reaction between two H atoms, which are mobile in ice at 77°K, and whose recombination results in the stabilization of the two corresponding, leftover, OH radicals. The H-H reaction probability is calculated in terms of the probability of escape of an H from a reactive volume, V_R (which encloses the formation sites of the H-OH radical pair), under conditions of an increasing background concentration of trapped OH. Two additional assumptions required are that the trapped OH radicals are spatially arranged according to a Poisson distribution and that H-H reactions are greatly favored over H-OH reactions during irradiation at 77°K. The final mathematical form of the OH-formation function can be shown to be

$$\exp \left\{ K(OH) \right\} = 1 + \frac{K}{W} I \quad (1)$$

in which

(OH) represents the OH concentration after a given irradiation dosage

I is the total irradiation dosage

$\frac{1}{W}$ is the probability of escape of an H atom from an isolated site of $\frac{1}{W}$ pair formation, of volume V_R

and

$$K = \frac{V_R}{V_T} \left(1 - \frac{1}{W} \right)$$

where V_T is the total volume.

The solid curves of Figure 2 are based on Equation (1) and are not empirically fitted curves. Only one arbitrary constant (K) was determined empirically, in each case, because the limiting slope is proportional to $1/W$. Figure 2 shows that the agreement between the experimental points and the curve obtained from Equation (1) is excellent for γ -irradiation; there is slightly less agreement for β -irradiation. The difference between the two curves may be ascribed to the difference in the energies of the electrons responsible for radical production in β - and γ -irradiation.

It has been shown (Ref. 26) that the average distance between radical-production sites decreases with the decreasing energy of β -irradiation. Thus, in the γ -irradiation experiments, where the energy of the primary electron responsible for radiation damage is 500 Kev, the average distance between radical-formation sites is considerably greater than in the β -irradiation experiments, where the electron energy is only 5.7 Kev. A 500-Kev primary electron from γ -irradiation that has been degraded to 5.7 Kev is, of course, indistinguishable from the 5.7-Kev β -particle from tritium. However, the degraded primary electron represents only about 1% of the gross effects in γ -irradiation. Consequently, the reactive volume (V_R), which enters into Equation (1) by way of the constant K, is much smaller in the case of soft β -irradiation because the local concentration of H is higher, as a result of the more closely spaced ionization spurs.

c. H and D Yields in γ -Irradiated H_2O , D_2O , and "Mixed" Ice at $4.2^\circ K$

In Ref. 21 an isotope effect was reported in the relative yields of H and D in the γ -irradiation of a 20%- H_2O , 80%- D_2O mixture at $4.2^\circ K$. Instead of the ratio of 4 expected for the intensities of the D-atom and H-atom signals, the ratio was found to be about 1.5. It was suggested that the isotope effect was an indication of the preferential breaking of an OH bond in HOD.

A detailed investigation of the isotope effect led to several surprising results. A study of the relative yields of H atoms in H_2O and D atoms in D_2O indicated that the isotope effect is probably attributable

to a difference in the efficiency of H- and D-atom production by γ -irradiation at 4.2°K. Moreover, it was found that the H-atom signal is much more saturated than the D-atom signal in the "mixed" ice, even though the EPR signals of H and D atoms stabilized in pure H₂O and D₂O matrices, respectively, have similar saturation properties with respect to microwave power.

A paper describing the detailed results of these investigations is being prepared for publication.

2. Properties of Radicals in Irradiated Ice at Low Temperatures

a. OH-Radical Decomposition at 77°K

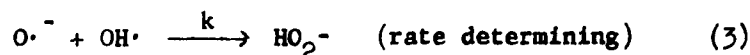
(1) Background

The isothermal decomposition of OH radicals in γ -irradiated ice in the temperature range from 77 to 108°K is described in detail in Refs. 2, 6, and 16. The OH decomposition was found to follow a 3/2-order-reaction rate law with a rate constant of $K = 3 \times 10^{11} \exp(-6000/RT)$ (moles/liter)⁻¹ sec⁻¹.

As in the tests with ice samples γ -irradiated by an external Co⁶⁰ source, the rate of OH-radical disappearance from internally β -irradiated tritium-enriched ice was found to be adequately described by a 3/2-order-reaction rate law. Moreover, the rate constants and activation energy for the decomposition are in good agreement with the previous results; thus, the differences, if any, in the spatial distribution of radicals formed by internal β - and external γ -irradiation do not noticeably affect the decomposition kinetics.

(2) Rate-Law Mechanism

The following mechanism was developed to describe the 3/2-order-reaction rate law for the disappearance of OH radicals:



The principal assumption incorporated in this mechanism is that $\text{OH}\cdot$ undergoes equilibrium dissociation as an acid and that it is a stronger acid than H_2O_2 . The experimental evidence available at present on the acidity of $\text{OH}\cdot$ pertains to aqueous liquid systems, and therefore is not strictly applicable in ice (Ref. 27). However, estimates of the relative acidity of $\text{OH}\cdot$ and H_2O_2 in liquid water (Refs. 28 and 29) give $\text{OH}\cdot$ an acidity approximately equal to or greater than that of H_2O_2 . The rate of disappearance of $\text{OH}\cdot$ can be written [from Reaction (3)] as

$$\frac{d(\text{OH}\cdot)}{dt} = -k (\text{O}\cdot^-)(\text{OH}\cdot) \quad (5)$$

With the assumption that $\text{OH}\cdot$ is a stronger acid than H_2O_2 , and therefore that most of the protons in the system come from the dissociation of $\text{OH}\cdot$, the equilibrium constant for Reaction (2) may be written as

$$(\text{O}\cdot^-)(\text{H}^+) = (\text{O}\cdot^-)^2 = K_a (\text{OH}\cdot) \quad (6)$$

or

$$(\text{O}\cdot^-) = K_a^{1/2} (\text{OH}\cdot)^{1/2} \quad (7)$$

Substituting Equation (7) into Equation (5),

$$\frac{d(\text{OH}\cdot)}{dt} = -kK_a^{1/2} (\text{OH}\cdot)^{3/2} = -K'(\text{OH}\cdot)^{3/2} \quad (8)$$

which is of the same form as the experimentally determined rate law.

In samples containing large concentrations of H_2O_2 , the concentration of H^+ would be approximately constant during the reaction if the main source of H^+ were now the equilibrium expressed by Reaction (4) rather than Reaction (2). The concentrations of H^+ and $\text{O}\cdot^-$ would then no longer be equal [Equation (6)], and the equilibrium expression for Reaction (2) would become

$$(\text{O}\cdot^-) = K_a \frac{(\text{OH}\cdot)}{\text{H}^+} = K' (\text{OH}\cdot) \quad (9)$$

Substitution of this result into Equation (5) yields

$$\frac{d(\text{OH}\cdot)}{dt} = -kK' (\text{OH}\cdot)^2 = -K''(\text{OH}\cdot)^2 \quad (10)$$

Thus, the proposed mechanism also predicts the observed experimental result for ice containing H_2O_2 (Refs. 2 and 16) - namely that the rate of disappearance of OH radicals follows a second-order-reaction rate law for sufficiently large concentrations of H_2O_2 .

(3) Experimental Results

In an attempt to test the proposed mechanism, a series of experiments were conducted on acidic ice. Dilute solutions (10^{-2} M) of HF and HCl were frozen into the EPR cavity at 77°K and were γ -irradiated at this temperature for 15 to 20 hr by an external Co^{60} source. The concentration of OH radicals after irradiation was approximately 10^{-4} M. The sample was then warmed to 100°K . The rate of disappearance of the OH radicals was measured by observing the decrease in intensity of the OH-radical EPR signal with time. Invariably, the decomposition was found to follow a $3/2$ -order-reaction rate law with the rate constants identical, within experimental error, to those observed in the pure-ice system.

Several additional experiments were performed, substituting NaOH and NH_4OH (10^{-2} M in water) for HF and HCl. Again, the results were the same - namely, the decomposition of OH followed a $3/2$ -order-reaction rate law with the same rate constants (to within experimental error) as those of the pure-ice system. Assuming the proposed mechanism, NaOH and NH_4OH as bases should have accelerated the equilibrium dissociation of OH expressed by Reaction (2), thereby accelerating the overall rate of reaction. Attempts to modify the matrix by including methanol (10^{-2} M in water) in the ice again gave the $3/2$ -order-reaction rate law with no measurable effect on the absolute rate.

The same $3/2$ -order-reaction rate law and rate constants observed for the disappearance of OH in the pure ice and in the ice containing the various additives cast serious doubt on the validity of the

proposed mechanism. According to the proposed mechanism, the disappearance of OH in the HF-ice and HCl-ice systems should have followed a second-order-reaction rate law. Moreover, the NaOH-ice and NH_4OH -ice systems should have had larger rate constants than those observed in pure ice for the disappearance of OH. However, before accepting the results of the acidic- and basic-ice experiments as valid tests of the proposed mechanism, three important questions must be raised:

To what extent are HF, HCl, NaOH, NH_4OH , and CH_3OH soluble in ice at 77°K?

How are the ionic dissociations of these species affected by the crystalline fields in the ice matrix?

What is the ion mobility in ice at the temperatures of interest?

Some conductivity data are available in the literature with reference to ion mobilities in ice (Ref. 27), and some conductivity measurements on the HCl-ice and pure-ice systems were made in the laboratory. These conductivity measurements indicate a small ion mobility in the HCl-ice system at 100°K, considerably larger mobilities being observed at $T > 120^\circ\text{K}$. Hydrochloric acid must be "soluble" in ice at low temperatures to some extent (probably 10^{-2} M or more), because the conductivity of HCl-ice was very much greater than that of pure ice at a given temperature.

However, these data alone do not indicate whether individual HCl molecules are frozen into the crystal lattice of ice (i.e., whether ice and HCl form a compatible solid solution) or whether the HCl is frozen out of the ice matrix but is trapped in widely separated, crystal-defect sites. (The proposed mechanism requires that the acid form a solid solution with ice in order to assure second-order-reaction kinetics). Moreover, these results can hardly be applied to other systems considered here. The conductivity measurements give positive evidence of high ionic dissociation and mobility in ice at low temperatures. What this evidence means is questionable, in view of the fact that the extent to which HCl and ice form solid solutions is not known.

b. Radical Formation and Decomposition in Ice Between 4.2 and 77°K

(1) Formation of Trapped Radicals in Ice by γ -Irradiation at 4.2°K

The formation of trapped OH radicals in ice at 77°K as a function of γ -irradiation dosage is described above. Hydrogen atoms are also produced by the irradiation at liquid-nitrogen temperature (77°K), but are not trapped in detectable amounts. However, the irradiation of ice at liquid-helium temperature (4.2°K) produces an EPR spectrum containing a 500-gauss doublet, which is characteristic of hydrogen atoms (see Figure 3). Most of the formation studies performed during the past 2 years were conducted at 4.2°K in order to determine the H-atom yields and to obtain information on the relative efficiencies of formation of OH at 4.2 and 77°K.

Irradiation at 4.2°K imposes some experimental limitations that were not involved in the studies made at 77°K. Because of the extremely low heat of vaporization of liquid helium (~ 1 cal/cc), only about 4 hr of continuous irradiation could be carried out before it became necessary to refill the Dewar vessel with liquid helium. As a consequence, the formation studies at 4.2°K were carried to saturation-radical concentrations, as was done at 77°K, where saturation was reached with irradiation times in excess of 100 hr. In addition, severe problems related to microwave-power saturation at the lower temperatures make it difficult to obtain accurate quantitative data at a low radical concentration. Finally, the familiar 77°K spectrum of the OH radical is noticeably altered in shape at 4.2°K and is interfered with by other underlying spectra, except at the lowest microwave powers available.

For γ -radiation dosages up to about 400,000 rep, the stabilized H and OH concentrations at 4.2°K were approximately equal and increased in a nearly linear fashion with increasing dosage (see Figure 4). The initial slope at 4.2°K was found to correspond to radical yields of $G_H \cong G_{OH} \cong 0.8/100$ ev, as contrasted with $G_{OH} \cong 0.6/100$ ev at 77°K (initial slope). These values are considerably lower than those previously reported (Refs. 2 and 21); the difference results from a combination of an earlier computational error and certain refinements in the technique of absolute concentration determination.

In addition to the spectra of H and OH, a broad line was observed at 4.2°K at a much lower field ($g = 2.08$) than the center of the OH spectrum. This line was not observable upon warming to 77°K, but reappeared upon recooling to 4.2°K; thus, the disappearance was reversible and was not caused by chemical decomposition. This line is not as susceptible as the OH spectrum to power saturation; at sufficiently low power levels, the relative peak heights indicated that the concentration of the new species was only about one-tenth as large as the concentration of H and OH. The broad line was observed at 4.2°K whether the irradiation was carried out at 4.2 or 77°K.

(2) Radical Reactions in γ -Irradiated Ice Between 4.2 and 77°K

Because of the similarity between radical-stabilization yields at 4.2 and 77°K, it was of considerable interest to investigate the fate of H atoms when a sample of ice is irradiated at 4.2°K and is then warmed to 77°K. In particular, it was apparent that it should be possible to investigate the relative rates of the two competing H-atom destruction reactions [Reactions (11) and (12), below] by observing the fraction of the OH destroyed when the ice was warmed to 77°K.

The most probable decay reactions during warmup are



The reaction of two OH radicals to form H_2O_2 is not included, because the OH radicals are not mobile between 4.2 and 77°K. As a first approximation, k_1 can be assumed to be equal to $2 k_2$, and the rate laws can be written as

$$-\frac{d(\text{H})}{dt} = 2 k_2 (\text{H})^2 + k_2 (\text{H}) (\text{OH}) \quad (13)$$

$$-\frac{d(\text{OH})}{dt} = k_2 (\text{H}) (\text{OH}) \quad (14)$$

If time is eliminated from Equations (13) and (14) and the resulting equation is integrated, the following expression can be obtained:

$$X = \left[\frac{X_o + 1}{(\text{OH})_o} \right] (\text{OH}) - 1 \quad (15)$$

where $X = (\text{H})/(\text{OH})$ and $X_o = (\text{H}_o)/(\text{OH}_o)$. As the temperature (T) approaches 77°K during warming, X approaches 0. Therefore, at 77°K, Equation (15) becomes

$$(\text{OH})_{77^\circ\text{K}} = \frac{(\text{OH})_o}{X_o + 1} \quad (16)$$

The OH concentration at 77°K predicted by Equation (16) and the experimentally determined OH concentrations obtained by successive irradiations at 4.2°K are compared in the tabulation below. Observations were made at 4.2 and 77°K, and the concentrations below are given in arbitrary units.

Concentrations at 4.2°K		Concentrations at 77°K	
(H) Experimental	(OH) Experimental	(OH) Calculated	(OH) Experimental
1	1	0.5	0.5
1.33	1.83	1.06	1.02
1.75	2.81	1.74	1.60
2.71	2.45	1.88	1.72

From the close agreement shown, it may be inferred that Equations (13) and (14) adequately describe the rate of the decay process under the given assumptions. The slightly lower experimental values found for $(\text{OH})_{77^\circ\text{K}}$, as compared to the calculated values, probably result from the fact that the ratio $k_1/2k_2$ is somewhat greater than unity.

The surprising result is that the buildup curve of OH produced by irradiation at 77°K is closely approximated by irradiating at 4.2°K and warming to 77°K. This result becomes even more puzzling in view of the rate equations given above. On the basis of those equations, which successfully describe the reactions of the radicals during the warmup period, the yield

of stabilized OH produced by irradiation at 77°K should be considerably less than the yield of OH produced by irradiating first at the lower temperature. It may be that the value of the rate constant for disappearance of H at 77°K is low enough that a sizeable steady-state concentration of H exists during irradiation at 77°K. The extrapolated value of the rate constant for H disappearance at 77°K (from the isothermal-rate-constant determinations between 20 and 50°K) would permit a steady-state concentration of H as high as 10^{-4} M to decay to less than detectable levels (10^{-6} M) in the 5-min period between cessation of irradiation and observation of the EPR spectrum. In addition, there must be only a limited number of paths for the movement of H atoms through the ice matrix. These must be labyrinth-type paths so that the H atoms do not move appreciably far from the point of initial formation within a reasonable length of time. Consequently, there should be a greater probability of reaction between radicals within a given (intra) spur than for radicals from different (inter) spurs. Thus, the model predicts that the reactions that take place in a finite time at 77°K are the same reactions (in a more-or-less one-to-one correlation) that take place during the warmup period between 4.2 and 77°K. The fact that the OH buildup curve is not affected by successive irradiations or by appreciable contaminant concentrations tends to support this view.

(3) Kinetics of Disappearance of H Atoms in Irradiated Ice

A detailed kinetic study of the disappearance of H atoms in γ -irradiated ice was also conducted. In the first method used, the ice was irradiated at 4.2°K to produce the trapped H atoms, and the change in intensity of the EPR spectrum was then observed as the H atoms disappeared during slow warming to 77°K. A careful analysis of several continuous warming curves of H concentration vs time and temperature failed to yield a self-consistent activation energy and order of reaction applicable over the entire range of temperatures studied.

In order to obtain the isothermal kinetic data required for independent determination of the order of reaction, it was necessary to devise a method of controlling the temperature of the EPR sample cavity at

points between 4.2 and 77°K. This control was accomplished by means of a slow stream of cold, boiloff gas from a helium-storage Dewar vessel used in conjunction with an intermittent, automatically controlled, electrical heater. This control system is described in detail in Ref. 17. The temperature was held to within $\pm 0.2^\circ\text{K}$ for up to 1 hr at temperatures from 20 to 60°K.

Unsuccessful attempts were made to observe directly the disappearance (due to reaction with H) of OH below 77°K, because the shape of the OH spectrum changed sufficiently during warming to preclude the quantitative determination of relative OH concentrations at different temperatures. However, previous studies in this laboratory (Ref. 18) indicated that the relative rate constants for the $\text{H} + \text{H}$ and $\text{H} + \text{OH}$ reactions are of comparable magnitude between 4.2 and 77°K. The $\text{OH} + \text{OH}$ reaction is immeasurably slow in this temperature range.

In an effort to determine independently the order of reaction and the activation energy, a number of rate measurements were made under isothermal conditions at several temperatures. In each of two series of experiments, the irradiated sample (irradiation dosages of 1 to 2×10^{19} ev/g were used, yielding radical concentrations of the order of 10^{-4} mole/liter) was warmed from 4.2°K in a stepwise fashion, and the concentration of H was followed as a function of time during several consecutive isothermal periods at successively higher temperatures. The results are plotted in Figure 5. For convenience in presenting the data, the zero of the time scale for each isothermal portion of a run was selected to coincide with the first experimental point taken after the attainment of a new constant temperature. The dependence of the isothermal rate on the total concentration of H is much too great to correspond with a normal rate law of the form $d(\text{H})/dt = k(\text{H})^n$. Instead, at each temperature, the initial rapid rate of disappearance seems to approach slowly an asymptotic value long before all the atoms have disappeared.

One of the factors that complicated the separation of variables in these studies was the dependence of the H-atom signal intensity on temperature. The intensity of EPR signals normally varies with the inverse of the absolute temperature. However, because of saturation effects, the H-atom

signal increased by a factor of about 2 between 4.2 and 20°K instead of decreasing by the expected factor of 5. Intensity decreased above 20°K, but a portion of the decrease was due to chemical reaction. It was essential, for comparisons between kinetic data obtained at different temperatures, that the temperature dependence and time dependence of the signal intensity be separable quantities. The approach to limiting atom concentration at each particular temperature became an advantage in attaining this end, because it was possible to warm the system to a desired maximum temperature (e.g., 40°K), to wait until reaction essentially stopped, and then to obtain a time-invariant temperature dependence down to 4.2°K for the signal from the remaining, nonreactive atoms. An empirical correction curve was made from data obtained in this manner for use in evaluating the kinetic data over the temperature range studied.

In view of the uncertainty in the dependence of the isothermal rate on the total H-atom concentration, comparisons between rates at two temperatures become significant only for constant concentrations. Even this type of comparison was found to yield different values for the activation energy, depending on the particular reference concentration selected, but the values obtained are much higher than 0.1 kcal/mole, and there is a distinct trend toward a higher activation energy at the higher temperatures. Comparisons of the rate toward the end of a run at one temperature with the rate at the beginning of the run at the next higher temperature (at essentially the same total concentration) yield activation energies ranging from somewhat less than 1 kcal/mole near 30°K to nearly 2.5 kcal/mole near 50°K. If the distribution of radicals were spatially isotropic, the temperature dependence of the apparent activation energy would suggest that the H atoms are stabilized in a variety of different trapping sites, with a range of energies for de-trapping and reaction.

Previous investigations in this laboratory (Refs. 16 and 19) led to the conclusion that the reactions occurring in irradiated ice between 4.2 and 77°K may be primarily intra-spur reactions, rather than isotropic processes. Supporting this explanation is the observation that the fractional rate of disappearance during continuous warming was independent of the initial concentration of H. For a variation of a factor of 4 in the initial

concentration, the disappearance curves were completely superimposable when the concentration was expressed as a fraction of the initial concentration and when the warming rate was the same in both cases. This, also, is precisely what would be expected if intra-spur reactions due to strong spatial correlations are dominant (Ref. 30), because inter-spur reactions would tend to yield ordinary, second-order-reaction kinetics. Actually, the data from the run at 49.9°K can be represented fairly well by a second-order-reaction rate expression, after the first four or five points. This fact is consistent with the expectation that inter-spur reactions should become more important in the very last stages of the disappearance, after most of the closely coupled radical pairs have disappeared.

A few kinetic experiments were conducted with D atoms in γ -irradiated D_2O , in an effort to obtain additional information about the mechanism through determinations of isotope effects. This study was also complicated by a peculiar variation of signal with temperature; in addition, the closer spacing of the D-atom lines (about 80 gauss) resulted in some interference from other underlying spectra. A preliminary evaluation of the data indicated no major difference between the D-atom and H-atom disappearance rates above 30°K - i.e., no unusually large isotope effects at the higher temperatures. Comparison of the data below 30°K will require a separate study of D-atom signal intensity as a function of temperature in the absence of chemical reaction, as was done for the H-atom system.

C. FORMATION AND DECOMPOSITION OF RADICALS IN OTHER SOLID MATRICES

In addition to the investigations performed with irradiated ice, a series of exploratory studies were undertaken on a variety of different solid-matrix systems. The experimental techniques were similar to those used in the ice investigations except as described below.

1. Studies of NF_2 Radical

a. Background

The NF_2 radical was chosen for special emphasis for several reasons. The extent of hyperfine interaction with fluorine nuclei in organic fluorocarbon radicals has been the subject of several investigations,

and it would be a valuable contribution to the new field of N-F chemistry if both the nitrogen and fluorine hyperfine-splitting constants for NF_2 were available. The EPR spectrum of NF_2 had not been reported in the literature at the time this work was under consideration. (Recently, Colburn, et al., have reported the EPR spectrum of NF_2 radicals in Ref. 31.)

It was expected that EPR observations of gaseous NF_2 in equilibrium with N_2F_4 would give an independent value for the N-N bond strength in the dimer. The gaseous NO_2 - N_2O_4 equilibrium is readily observable by EPR techniques at pressures of a few millimeters of mercury.

Finally, and perhaps most important, it was also hoped that the reactivity of NF_2 radicals could be studied if a suitable solid matrix were found so that the radicals would be trapped or partially stabilized.

b. Condensation-Trapping Experiments

It has frequently been observed that a purple or red color is obtained in the normally white solid when N_2F_4 is rapidly condensed from room temperature to 77°K . It was thought that this color might be due to trapped NF_2 radicals. In fact, it was observed that the color was intensified greatly if the N_2F_4 was passed at low pressure (less than 1 mm Hg, estimated) through a hot (300 to 500°C) quartz tube and allowed to condense at 77°K .

Even when the solid so obtained had a very intense, deep purple color, EPR observations made at 77°K failed to yield spectral peaks. Thus, the purple color must be derived from a source other than NF_2 radicals.

Further investigations showed that some of the purple color persists in the liquid when the purple solid is allowed to melt. This observation corroborates the conclusions reached above because it is to be expected that NF_2 radicals, if present, would recombine rapidly in liquid N_2F_4 , with the major diffusion barrier of the solid trapping matrix no longer present.

c. Photolysis of Solid N_2F_4

The second approach used in the search for NF_2 radicals employed the irradiation with ultraviolet light (2537 \AA) of solid N_2F_4 in a quartz tube at 77°K while in a multipurpose cavity.

A very slight discoloration of the N_2F_4 occurred in these experiments, but again no spectrum was obtained. The energy of light quanta at the wavelength employed is several times that required to break the N-N bond in N_2F_4 .

d. Gas-Phase Experiments

In order to test the sensitivity of the EPR equipment for gaseous radicals, a preliminary experiment was conducted at room temperature with gaseous NO_2 - N_2O_4 . At the selected experimental pressure of 5 mm Hg, dissociation into NO_2 is essentially complete at room temperature. No difficulty was experienced in obtaining a full-scale EPR signal consisting of the nearly resolved hyperfine triplet (48-gauss separation) that results from interactions of the odd electron with the N^{14} nucleus ($I = 1$). Higher pressures cause serious broadening of the signal and corresponding loss of resolution (Refs. 32 and 33). One of the NO_2 spectra is shown in Figure 6.

It was expected that gaseous NF_2 would show a similar N^{14} triplet with a possible F^{19} doublet structure superimposed. Several experiments were conducted in which quartz tubes containing gaseous N_2F_4 were placed in a multipurpose EPR cavity, and a search was made for spectra that might be caused by NF_2 radicals. One experiment was performed at room temperature with the N_2F_4 at near-atmospheric pressure. Other experiments were performed at N_2F_4 partial pressures of 4 to 5 mm Hg and at temperatures ranging from ambient to 120°C.

In no case was an EPR signal observed, except for some small background peaks well away from the $g = 2$ region; these peaks were subsequently shown to originate in the quartz sample tube. The search was not restricted to the vicinity of $g = 2$, although that might appear to be the most likely value for NF_2 , but covered a region from approximately $g = 0.7$ to $g = 10$. It is believed that as little as 1 to 2% equilibrium dissociation of the N_2F_4 to form NF_2 would have been detected.

e. Conclusions

Because NF_2 radicals have been observed elsewhere (Ref. 31), it is reasonable to assume that either the NF_2 sample used here contained impurities

that may have combined with the NF_2 radicals to form nonradical species, or that reaction with the quartz vessels containing the samples was important. Some etching was observed in all the vessels after the experiments.

2. Studies of Irradiated Solid Ammonia

A sample of anhydrous liquid NH_3 was frozen into the microwave cavity and was irradiated for 1.5 hr at 4.2°K . The EPR spectrum (Figure 7a) consisted of (a) three broad lines separated by 25 gauss, and (b) a strong, broad background believed to be due to a trace of copper oxide removed from the cavity walls and dissolved in the ammonia. The sample was then allowed to warm to 77°K . At that temperature there was no evidence of the three-line spectrum; rather, a complex spectrum of at least 12 lines appeared (Figure 7b).

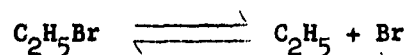
The complex spectrum is as yet unexplained; the three-line spectrum could be caused by splitting by a nitrogen nucleus ($\text{spin} = 1$) or by two protons. The relative intensities of the lines would permit a distinction between these cases (1:1:1 for N, 1:2:1 for 2H), but the spectrum is too poorly resolved for accurate determination of the relative intensities.

Although none of the radical species in the irradiated ammonia has been identified, it is clear that one radical was converted into another. The formation of the complex spectrum was shown to be an irreversible process because this spectrum persisted unchanged when the sample was recooled to 4.2°K .

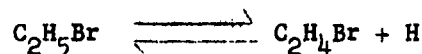
3. Studies of Ethyl Bromide, Methyl Iodide, Methanol, and Tetramethyltetrazine

a. Ethyl Bromide

The irradiation of solid $\text{C}_2\text{H}_5\text{Br}$ could conceivably produce at least three different primary alkyl radicals: $\text{CH}_3\dot{\text{C}}\text{H}_2$, $\text{CH}_3\dot{\text{C}}\text{HBr}$, or $\cdot\text{CH}_2\text{CH}_2\text{Br}$. It was thought that cage effects in the solid matrix might selectively inhibit the formation of $\text{CH}_3\dot{\text{C}}\text{H}_2$ (ethyl) radicals in relation to the other two possibilities. The bromine atom that must be lost to form the ethyl radical would experience greater difficulty in escaping from the matrix cage at the formation site than would the much smaller H atom, which is removed in the formation of either of the other two postulated species. Reversal of the reaction,



should occur with a higher probability than reversal of the other processes,



because of the greater ease or irreversible escape of H as opposed to Br.

A sample of practical grade $\text{C}_2\text{H}_5\text{Br}$ was γ -irradiated at 77°K in an exploratory experiment. The spectrum at 77°K (Figure 8a) consisted of nine, broad, widely spaced lines of undetermined origin. Interpretation of this spectrum will be complicated by the $3/2$ spin of the bromine nuclei (both Br^{79} and Br^{81}), which might interact in either of the $\text{C}_2\text{H}_4\text{Br}$ radicals. The spacing between lines of the broad spectrum is about 25 gauss, and the g-factor appears to be about 2.03; both values are subject to considerable uncertainty.

An unexpected result was obtained when the sample with the broad spectrum was warmed slowly to determine the temperature at which the spectrum disappeared. The spectrum remained essentially unchanged until the warming was carried to 150°K , which is only about 3 to 4°K below the melting point of pure ethyl bromide. The sample was held at this temperature for about 1 min and was then cooled to near 130°K for observation. The nine-line spectrum had faded appreciably, and a strong spectrum of ethyl radical was present (Figure 8b). The assignment of the new, sharp lines to the ethyl radical is based on a nearly perfect correlation with the quartet of triplets obtained by Smaller and Matheson (Ref. 34) after the photolysis of ethyl iodide in argon. In the symbolic ethyl-radical reference spectrum at the top of Figure 8b, lines having the same number are members of a triplet (e.g., 1a, 1b, and 1c), and lines having the same letter are members of a quartet (e.g., 1b, 2b, 3b, and 4b).

b. Methyl Iodide

The γ -irradiation of solid methyl iodide at 77°K produced a strong spectrum of methyl radicals, in agreement with the spectrum reported in Ref. 34. The methyl radicals were much less stable than the ethyl radicals, as might be expected. The methyl spectrum decayed rapidly at about 170°K , which is nearly 40°K below the melting point of the methyl iodide matrix.

Liquid methyl iodide was decomposed rapidly at room temperature to form iodine under the action of 2537-A ultraviolet radiation. However, the same radiation had almost no effect on solid CH_3I at 77°K . None of the expected $\text{CH}_3\cdot$ quadruplet was observed, although γ -irradiation at 77°K produces a strong methyl spectrum. Also, only a trace of I_2 was observed when the ultraviolet-irradiated sample was melted and warmed to room temperature. Cage effects were apparently almost 100% effective in preventing the diffusion of $\text{CH}_3\cdot$ and $\text{I}\cdot$ away from each other in the solid. Gamma-irradiation appears to furnish enough additional energy to permit the diffusion of radicals away from their formation sites.

A final surprising observation, which merits special attention, was the formation of stabilized H atoms, apparently on a surface of the quartz Dewar vessel, under the action of 3660-A ultraviolet light in the ultraviolet irradiation of CH_3I and CH_3OH and $(\text{CH}_3)_2\text{NNNN}(\text{CH}_3)_2$, described below. The quantum energy of electromagnetic radiation at this wavelength is only 78 kcal/mole, which is less than the energy required to break a normal O-H, C-H, or N-H bond. It is assumed that the H must come from some compound so strongly chemisorbed on the quartz that the principal chemical bond to H is appreciably weakened. Efforts to produce stable H on other pieces of moist quartz by ultraviolet irradiation at 77°K proved unsuccessful.

c. Methanol

(1) Experimental Discharge-Trapping Method

A technique was developed for the rapid transfer of the trapped products of a Tesla discharge from the cold trap into the EPR sample cavity. At its present stage of development this technique is somewhat crude, but some successful transfers have been accomplished and spectra have been observed with two materials, CH_3OH and $(\text{CH}_3)_2\text{NNNN}(\text{CH}_3)_2$.

The discharge apparatus is basically the same as that described in Ref. 2) except for the addition of a ground joint that permits removal of the liquid-nitrogen-filled cold finger with the trapped discharge products coating the outside of the finger. After collection of the products is completed, air is slowly admitted to the apparatus just prior to disassembly. This air impinges first on an uncoated part of the cold finger so that only precooled air

contacts the discharge deposit. The cold finger is then removed and the deposit is scraped off into the precooled sample cavity, using a razor blade that is kept cold by means of frequent dipping into liquid nitrogen. The remainder of the procedure for observation of the EPR spectrum is the same as that normally employed.

(2) Discharged Methanol

A sample of the dark red deposit obtained from discharged methanol (described in Ref. 2) was introduced into the EPR cavity by the method described above. The spectrum of this material (Figure 9) includes a fairly well resolved triplet, indicating that only two protons are interacting strongly with the odd electron. The hyperfine splitting (about 25 gauss) is normal for alkyl radicals. Species that might be responsible for this spectrum are CH_2^+ and CH_2OH . Several other experimenters have reported a similar triplet for methanol irradiated with ultraviolet or γ -radiation, and the general consensus appears to favor CH_2OH (Ref. 35).

The triplet spectrum has a very much greater thermal stability than that of the red portion of the methanol deposit; the red color disappeared rapidly at 100°K , while the triplet spectrum decomposed near 150°K . Thus, the red color and triplet spectrum are due to two different species, and the CH_2OH radical is shown to be nearly colorless.

The red portion has been found to be photochemically decomposed at 77°K by ordinary room illumination. Ultraviolet light at a wavelength of 3660 Å is extremely effective in destroying the color, and a slow decomposition was effected by red light through a filter with a cutoff at 6000 Å (photon energy ≈ 48 kcal/mole).

The most significant aspect of these findings is that the red material apparently decomposes chemically to produce a gas (probably H_2) and yet has no observable EPR spectrum at 77°K . A spectrum might be observable at 4.2°K , but it would be difficult to form a definite association between such a spectrum and the red color. At this point, it appears most reasonable to assume that the red color is due simply to a color center produced by a trapped electron or an electron deficiency that produces a chemical reaction upon warming.

(3) Ultraviolet-Irradiated Methanol

The EPR spectrum of 2537-A ultraviolet-irradiated methanol at 77°K was very strong but much more complex than that produced by γ -irradiation at the same temperature. Gamma-irradiation produced only a simple triplet, which has been attributed to $\cdot\text{CH}_2\text{OH}$; none of these lines could be observed in the spectrum of the ultraviolet-irradiated material.

Such behavior is precisely the opposite of that which might be expected, because the ultraviolet radiation is monochromatic at about the energy necessary to break a single chemical bond, whereas the secondary electrons produced by Co^{60} γ -rays have energies of 100 ev or more and might be expected to produce the wider variety of radicals.

d. Tetramethyltetrazine

(1) Discharged Tetramethyltetrazine

Tetramethyltetrazine $[(\text{CH}_3)_2\text{NNNN}(\text{CH}_3)_2]$ was passed through the discharge apparatus described above in the hope of trapping $(\text{CH}_3)_2\text{N}$ radicals, because the molecule is known to decompose to form N_2 and $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$, presumably through $(\text{CH}_3)_2\text{N}$ as an intermediate.

The EPR spectrum of the faintly blue discharge deposit is shown in Figure 10. The spectrum was fairly weak; it consisted of about nine lines, the central line being disproportionately large for a single species. The interpretation is uncertain, but there is no clear evidence for $(\text{CH}_3)_2\text{N}$, although the splitting is about right for alkyl protons; $(\text{CH}_3)_2\text{N}$ should give a triplet of septets, or a septet of triplets due to hyperfine splitting by one N and by six presumably equivalent protons. The resolution is too poor to permit a definite conclusion regarding the identity of the species.

An important observation on this material is that γ -irradiation of the sample at 77°K did not enhance the spectrum, nor did any new lines appear. Thus, the species responsible for the spectrum in Figure 10 is produced in the discharge but not by in situ irradiation. This situation could well be due to a cage effect in the solid, if the observed paramagnetic species is too large to diffuse rapidly away from its formation site in the cold solid.

(2) Ultraviolet-Irradiated Tetramethyltetrazine

Two attempts to produce $(\text{CH}_3)_2\text{N}$ radicals by the action of 2537-A ultraviolet light on tetramethyltetrazine at 77°K failed to produce an observable spectrum. However, one of these experiments was conducted with about a 5% solution of the tetrazine in methanol, and the normal complex methanol spectrum appeared with only about 1% of the intensity that was obtained with pure methanol.

These results make it apparent that the tetramethyltetrazine acted as a very efficient scavenger for the radicals responsible for the methanol spectrum.

V. PROJECT PERSONNEL

In addition to the authors, the following technical personnel contributed to the project during the 2-year period covered by this report: Dr. S. Skolnik,* Dr. B. Keilin, and Mrs. L. Baum.

*Dr. Skolnik was succeeded as Principal Investigator by Dr. Barsh on 14 March 1961.

LIST OF TECHNICAL NOTES

The Technical Notes previously published on the effort being reported are listed below.

A Versatile, 1000-Curie, Cobalt-60, Gamma-Ray Source, Aerojet-General TN-16 (AFOSR-TN-56-339, ASTIA Document No. AD 95215), July 1956.

Chemical Fragments as Ultra-Energy Propellants, Abstracts Bulletin No. 1, Aerojet-General Report 1284 (Special) (AFOSR-TN-57-408, ASTIA Document No. AD 132 486), July 1957.

Chemical Fragments as Ultra-Energy Propellants, Abstracts Bulletin No. 2, Aerojet-General TN-22 (AFOSR-TN-57-609, ASTIA Document No. AD 136 692), October 1957.

Chemical Fragments as Ultra-Energy Propellants, Abstracts Bulletin No. 3, Aerojet-General TN-25 (AFOSR-TN-58-223, ASTIA Document No. AD 154 125), March 1958.

Kinetic Studies of the Disappearance of Hydroxyl Radicals in Ice at Low Temperatures, Aerojet-General TN-31 (AFOSR-TN-59-539, ASTIA Document No. AD 216 556), August 1959.

Free Radical Fuels - A Tough Problem, Aerojet-General TN-32 (AFOSR-TN-59-821), September 1959.

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Temperature Control Method for Use Between 4.2 and 77°K, Aerojet-General TN-37 (AFOSR-TN-60-760), August 1960.

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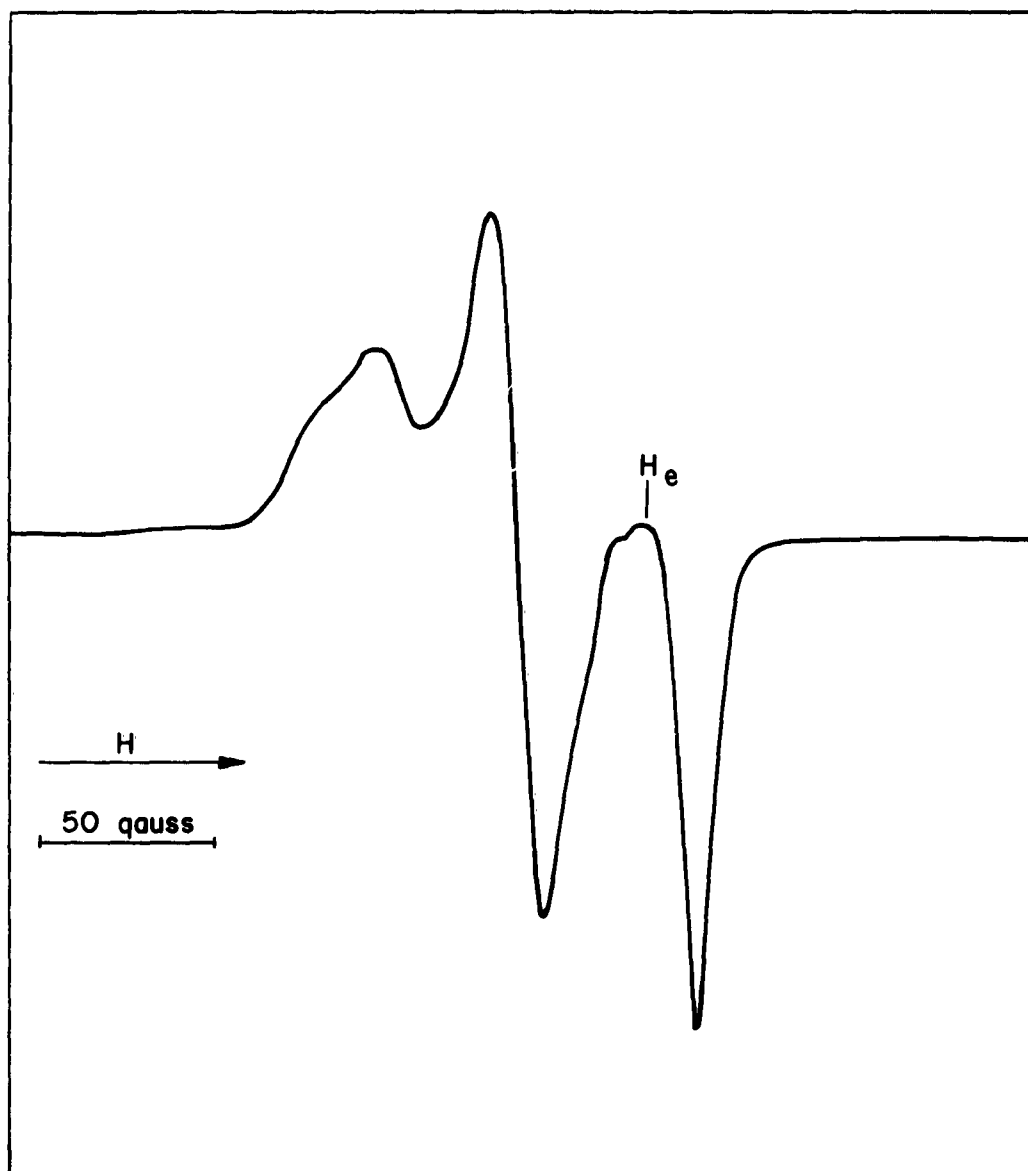
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EPR ABSORPTION DERIVATIVE SPECTRUM
OF β -IRRADIATED ICE AT 77°K

Figure 1

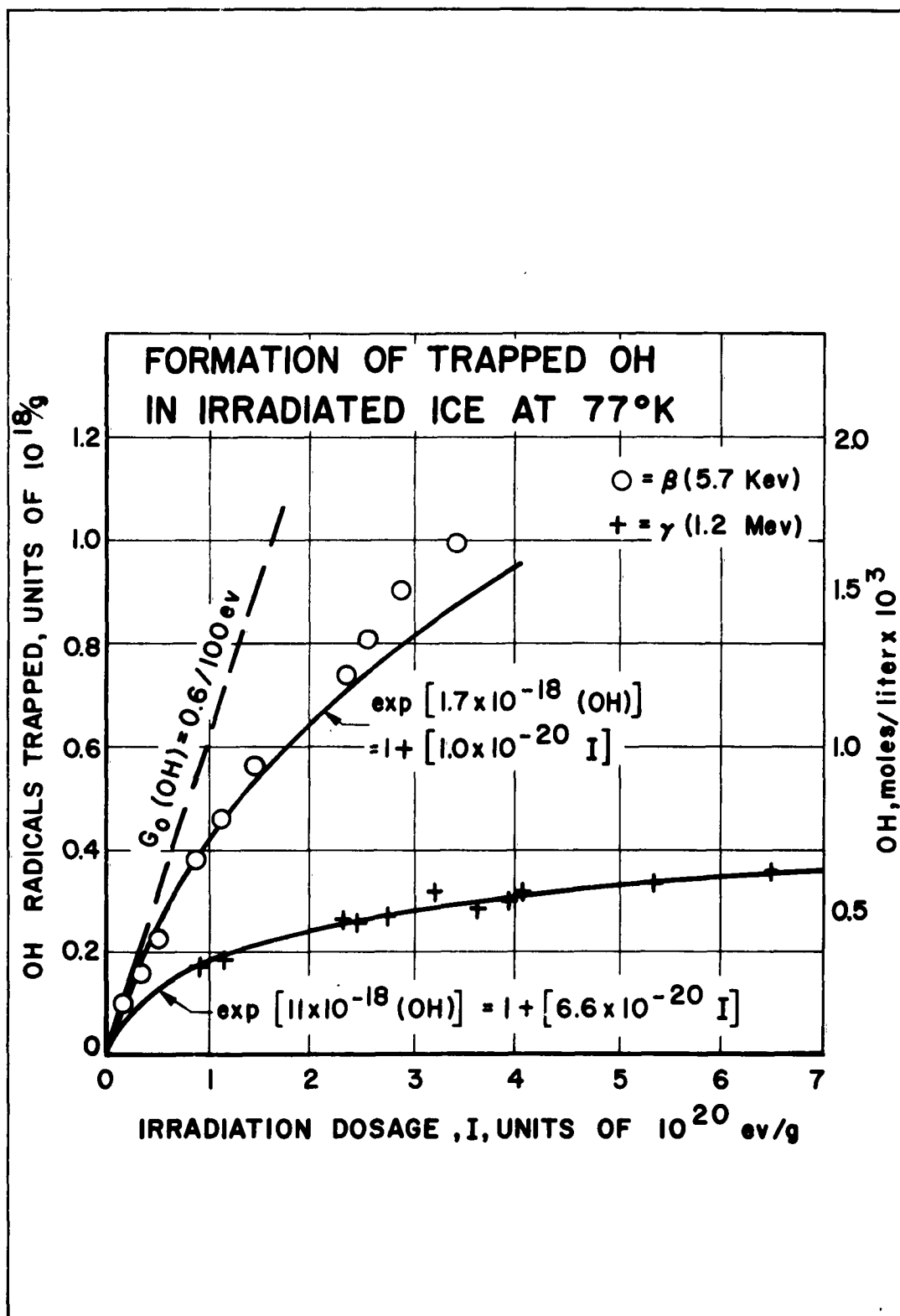
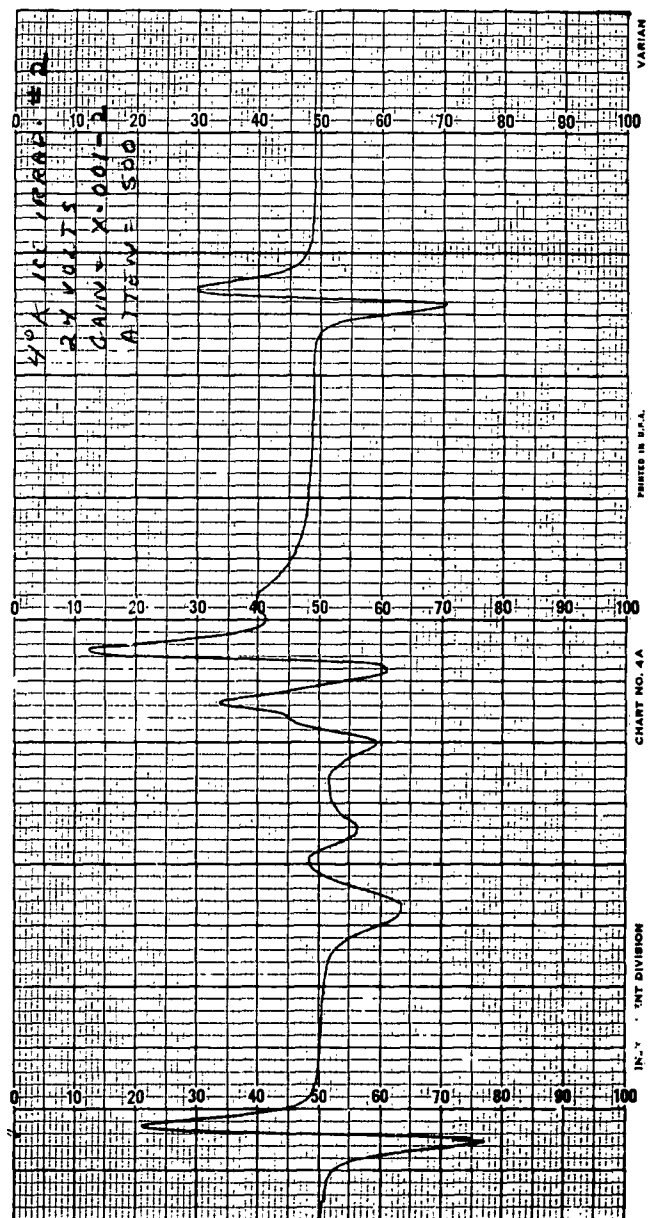


Figure 2



4.2°K Irradiated Ice

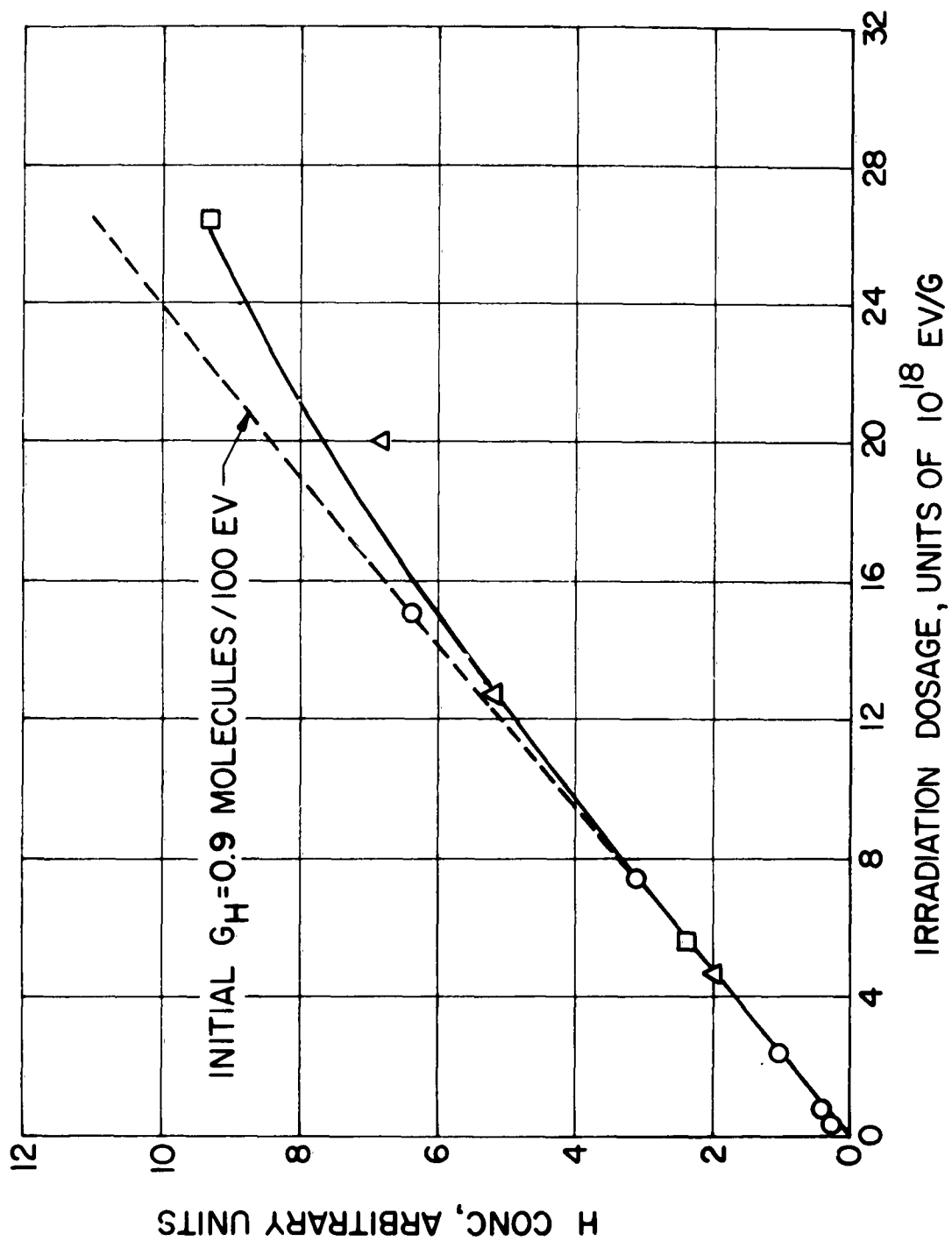
Stabilization of H Atoms in γ -Irradiated Ice at 4.2°K as a Function of Cumulative Dosage

Figure 4

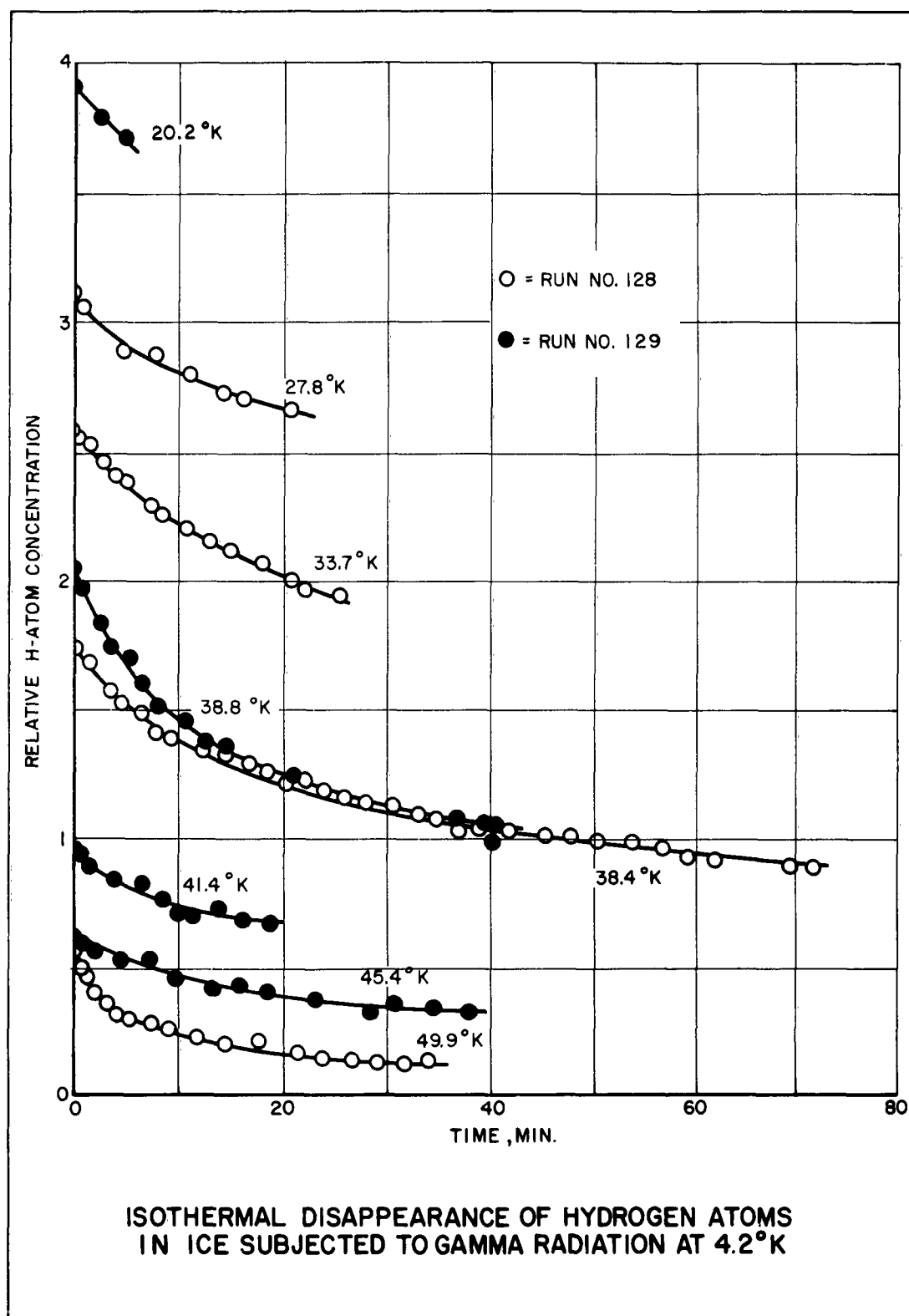
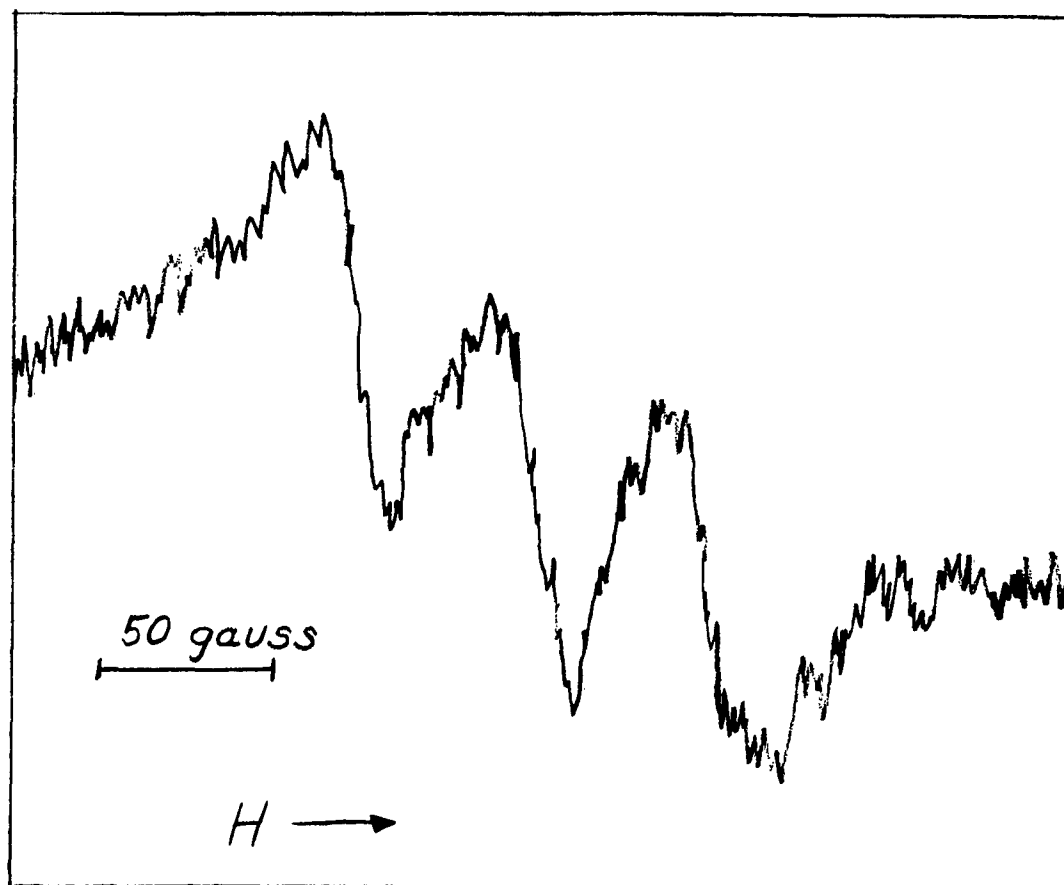
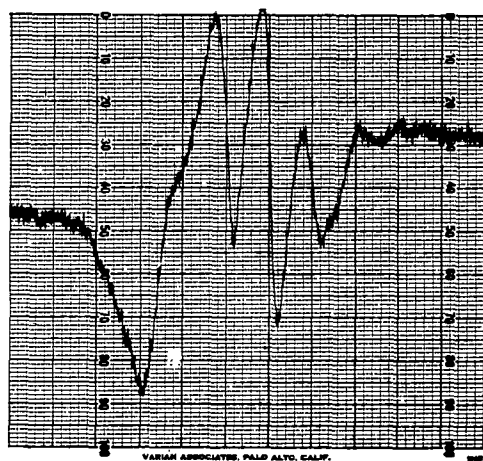


Figure 5

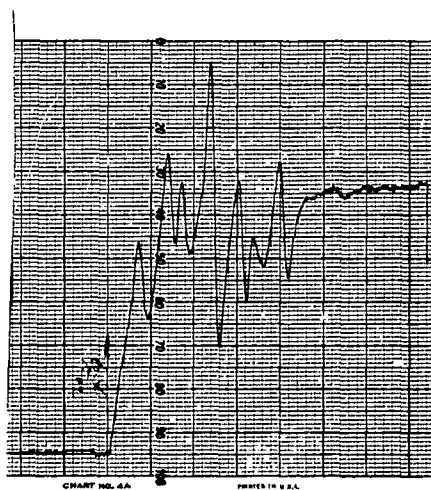


EPR Absorption Derivative Spectrum
Of NO₂ At 5mm Pressure

Figure 6



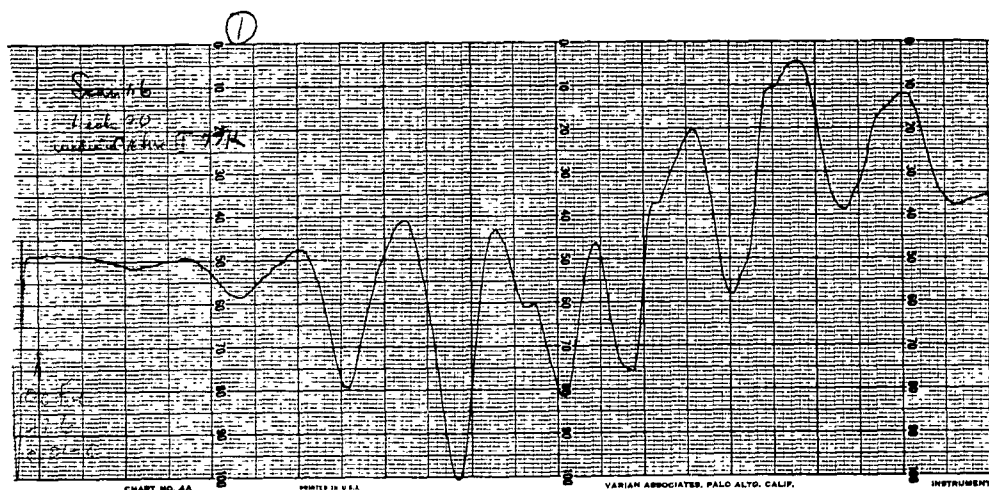
(a) Irradiated and Observed at 4.2°K



(b) Irradiated at 4.2° or 77°K and Observed at 77°K

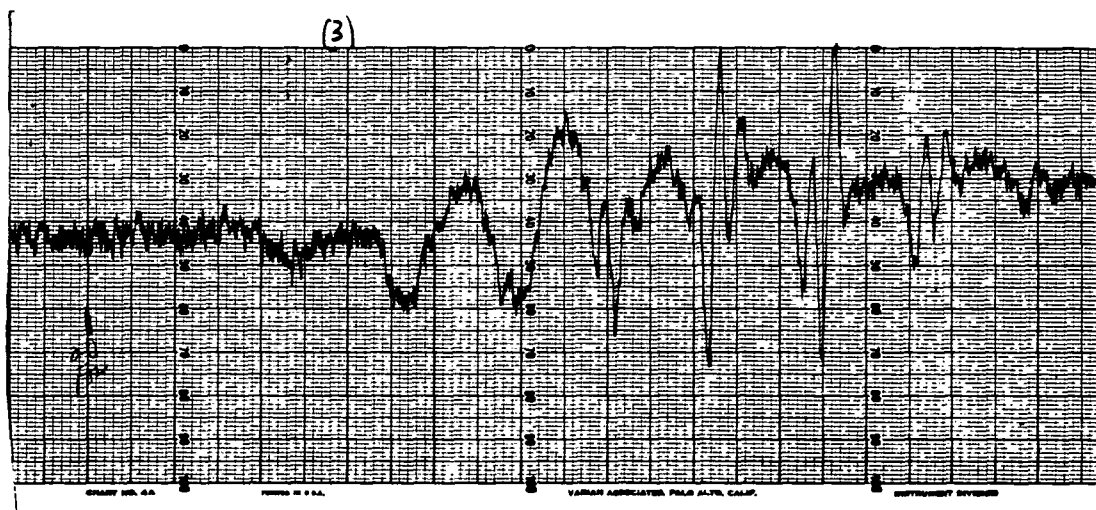
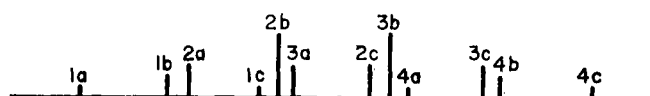
EPR Spectra of Gamma-Irradiated NH_3

Figure 7



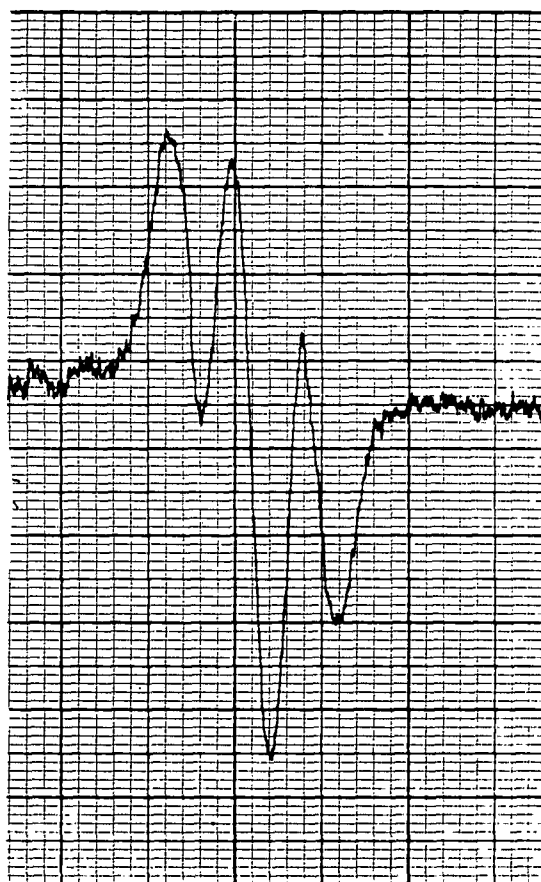
(a) Irradiated and Observed at 77°K

Ethyl Spectrum



(b) Irradiated at 77°K and Warmed to 150°K

EPR Spectra of Gamma-Irradiated Ethyl Bromide

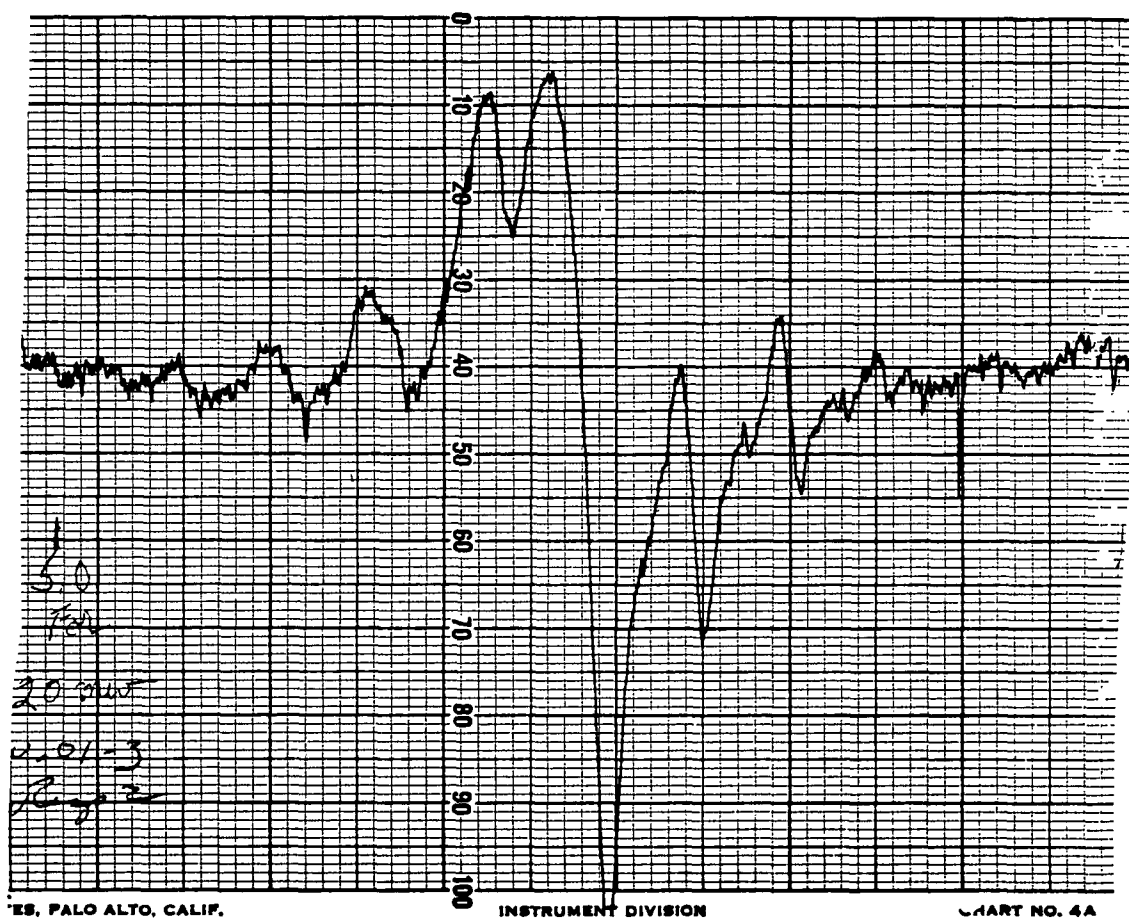


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CHART NO. 4A

EPR Spectrum of Methanol Discharge Products at 77°K

Figure 9



EPR Spectrum of Tetramethyltetrazine Discharge Products at 77°K

<p>Aerojet-General Corp., Azusa, Cal. KINETICS OF ENERGETIC SPECIES AT LOW TEMPERATURES, by H. S. Judeikis, M. K. Barsh, J. M. Flournoy, et al. November 1961. 39 p. illus. refs. (Proj. 9750; Task 37501) (Aerojet Report 2121; AFOSR-1758) (Contract AF 18(603)-110) Unclassified report</p> <p>Final report, 10/1/59 to 9/30/61</p> <p>Research during the past 2 years on the stabilization and subsequent chemical reactions of energetic free (over)</p>	<p>UNCLASSIFIED</p>	<p>UNCLASSIFIED</p>	<p>UNCLASSIFIED</p>
<p>Aerojet-General Corp., Azusa, Cal. KINETICS OF ENERGETIC SPECIES AT LOW TEMPERATURES, by H. S. Judeikis, M. K. Barsh, J. M. Flournoy, et al. November 1961. 39 p. illus. refs. (Proj. 9750; Task 37501) (Aerojet Report 2121; AFOSR-1758) (Contract AF 18(603)-110) Unclassified report</p> <p>Final report, 10/1/59 to 9/30/61</p> <p>Research during the past 2 years on the stabilization and subsequent chemical reactions of energetic free (over)</p>	<p>UNCLASSIFIED</p>	<p>UNCLASSIFIED</p>	<p>UNCLASSIFIED</p>

<p>radicals is summarized. Hydrogen atoms, hydroxyl radicals, and other normally unstable chemical species, produced by ionizing radiation and by electric discharges, were stabilized at low temperatures and were subsequently investigated. The rates of formation and disappearance of some of these radicals were measured over a range of temperatures by means of electron-paramagnetic-resonance techniques. Mechanisms are postulated to explain the observed rate phenomena.</p>	<p>UNCLASSIFIED</p>	<p>radicals is summarized. Hydrogen atoms, hydroxyl radicals, and other normally unstable chemical species, produced by ionizing radiation and by electric discharges, were stabilized at low temperatures and were subsequently investigated. The rates of formation and disappearance of some of these radicals were measured over a range of temperatures by means of electron-paramagnetic-resonance techniques. Mechanisms are postulated to explain the observed rate phenomena.</p>	<p>UNCLASSIFIED</p>
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